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(54) CATALYST FOR ALKYLENE OXIDE ADDITION REACTION

(57) Abstract:

PROBLEM TO BE SOLVED: To provide a catalyst for alkylene oxide addition reaction in which the catalytic activity is improved compared to a conventional catalyst, the catalytic filtering property is remarkably improved by significantly reducing the amount of the byproduct, and the amount of the unreacted component of the source material can be decreased compared to a conventional catalyst, and to provide a method for preparing the alkylene oxide adduct by using the aforementioned catalyst.

SOLUTION: The catalyst for alkylene oxide addition reaction contains a multiple oxide of Zn, Al and Mg, and the method for preparing an alkylene oxide adduct is carried out by using that catalyst.

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CLAIMS `

[Claim(s)]

[Claim 1] The catalyst for alkylene oxide addition reactions which comes to contain the multiple oxide of Zn, aluminum, and Mg.

[Claim 2] The catalyst according to claim 1 which are 0.1 <=(Zn+Mg)/aluminum(atomic ratio) <=10 and 0.001 <=Zn/Mg(atomic ratio) <=10.

[Claim 3] a catalyst precursor -- a general formula (I) -- the positive number with which $0.1 \le (1-x) / x \le 10$, and a and b fill $0.001 \le a/b \le 10$ among :[(Zna Mgb) 2+1-x aluminum3+x (OH)2]x+(An-) x/n and a mH2 O[type. An- shows the anion radical of n **. When A is plurality, n shows the total value of the valence of A. m is zero or more numbers.] The catalyst according to claim 1 come out of and expressed.

[Claim 4] a claim -- the manufacture approach of the alkylene oxide adduct which makes alkylene oxide add to the organic compound which has active hydrogen under existence of the catalyst of a publication one to 3 either.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the manufacture approach of the alkylene oxide adduct which uses the catalyst for alkylene oxide addition reactions, and this catalyst.

[0002]

[Description of the Prior Art] To the organic compound (henceforth an active hydrogen compound) which has active hydrogen, such as alcohol and a phenol, alkylene oxide As a catalyst used for the reaction to which it makes it add (it is hereafter called AO) For example, aluminum3+, Ga3+, In3+, Tl3+, Co3+, Sc3+, the catalyst (JP,1-164437,A --) which consists of a magnesium oxide with which a kind of the metal chosen from the group which consists of La3+ and Mn2+, or more than it was added The catalyst which consists of a 8-268919 official report and a baking hydrotalcite containing Mg2+ and aluminum3+ is known (JP,2-71841,A).

[0003] However, the multiple oxide catalyst which added and calcinated aluminum ion to the magnesium oxide currently indicated by JP,1-164437,A cannot say filterability as fitness the top where activity is very low, either. There are many amounts of generation of high molecular weight objects, such as a polyethylene glycol which furthermore carries out a byproduction. Although the multiple oxide catalyst which calcinated the Mg/aluminum hydro talc stone was indicated in JP,2-71841,A, the filterability were satisfied with effect with the high molecular weight object which cannot say that activity is still enough and carries out a byproduction of filterability was not acquired. Furthermore, by JP,8-268919,A, in order to reduce the load to a filtration process, the magnesium oxide / aluminum-oxide multiple oxide catalyst is indicated as a catalyst which raised activity. However, since the filterability of the catalyst itself was not good, the load to a catalyst separation process had the trouble that it was still great.

[0004]

[Problem(s) to be Solved by the Invention] Compared with the catalyst of (1) former, catalytic activity of the technical problem of this invention is improving. (2) Catalyst filterability can be raised by leaps and bounds by reducing sharply the amount of generation of the high molecular weight object as a by-product. (3) It is offering the manufacture approach of AO adduct which uses the catalyst for AO addition reactions and this catalyst which can reduce the unreacted part of the active hydrogen compound which is a raw material compared with the conventional technique.

[0005]

[Means for Solving the Problem] Namely, summary of this invention (1) In the catalyst for AO addition reactions and list (2) which come to contain the multiple oxide of Zn, aluminum, and Mg It is related with the manufacture approach of AO adduct which makes AO add to the organic compound which has active hydrogen under existence of the catalyst of the aforementioned (1) publication.

[0006]

[Embodiment of the Invention] The catalyst of this invention is a catalyst for AO addition reactions which consists of a multiple oxide of Zn, aluminum, and Mg. As for the atomic ratio of (Zn+Mg)/aluminum in the catalyst of this invention, 0.1 <= (Zn+Mg)/aluminum <= 10 are desirable from a viewpoint of catalytic activity, 0.5 <= (Zn+Mg)/aluminum <= 9 are more desirable, 1 <= (Zn+Mg)/aluminum <= 9 are still more desirable, and especially 1 <= (Zn+Mg)/aluminum <= 4 are desirable. Moreover, from catalytic activity and a filterable viewpoint, as for the atomic ratio of Zn/Mg, 0.001 <= Zn/Mg <= 10 are desirable, 0.01 <= Zn/Mg <= 1 is desirable. In addition, the catalytic activity said to this invention means the operation ability to the labile and selectivity of AO addition reaction.

[0007] moreover, from a viewpoint which makes the effectiveness of a request of this catalyst discover as a catalyst of this invention the catalyst precursor -- a general formula (I) -- the positive number with which 0.1 <= (1-x) / x <= 10, and a and b fill 0.001 <= a/b <= 10 among :[(Zna Mgb) 2+1-x aluminum3+x (OH)2]x+(An-) x/n and a mH2 O[type. An- shows the anion radical of n **. When A is plurality, n shows the total value of the valence of A. m is zero or more numbers.] It is desirable that it is the synthetic hydrotalcite compound [it is hereafter called a catalyst precursor (I)] which comes out and has the presentation expressed, and what calcinated this catalyst precursor (I) and was obtained is desirable. here -- (1-x) / x -- desirable -- 0.5-9 -- further -- desirable -- 1-9 -- it is 1-4 especially preferably. Moreover, a/b is 0.01-1 preferably [it is desirable and] to 0.01-5, and a pan. Moreover, n is the integer of 1-3 preferably. In addition, the structure of a catalyst precursor (I) is searched for by the X-ray powder diffractometry.

[0008] A preparation of catalyst> catalyst precursor is obtained as precipitate (compound hydroxide) by mixing the solution (henceforth metal ion content liquid) and alkali chemicals containing the ion of each metal of Zn, aluminum, and Mg at predetermined temperature.

[0009] Although the nitrate of each metal, acetate, a sulfate, a chloride, etc. may use any for preparation of metal ion content liquid, a filterable viewpoint to the catalyst engine performance,

i.e., catalytic activity, and the nitrate of a catalyst are desirable. As a solvent which dissolves a metal salt, organic solvents, such as a methanol besides water, such as ion exchange water usually used, ethanol, and ethylene glycol, may be used, and you may be such mixture. The anything which produces precipitate by mixing with metal ion content liquid, alkali chemicals are OH, for example, although it is good. - The compound which has ion, or the mixture or either which has An-ion is mentioned. When using as mixture, coincidence supply is respectively carried out as mixture of both compounds, and it is used for preparation of a catalyst precursor. As An-ion, the anion of at least one sort of oxygen acid chosen from S, Se, Te, P, Si, germanium, Sn, B, V, Cr, Mo, W, Mn, Ru, Rh, Os, and U or metal halogen acid, S2-, CO3 2-, or Cs3 2- is illustrated. From a viewpoint of catalytic activity, the mixture of a sodium hydroxide, and a sodium carbonate or a sodium sulfate especially a sodium carbonate is mentioned as desirable alkali chemicals. Although which gestalt of a solid or a water solution is sufficient as the supply gestalt of alkali chemicals, the homogeneous viewpoint of a reaction to its water solution is desirable.

[0010] It is OH in alkali chemicals to the quantitative ratio list of each metal ion of Zn, aluminum, and Mg in metal ion content liquid. - The quantitative ratio of the compound which has ion, and the compound which has An-ion will not be especially limited, if a desired catalyst precursor, as a result a desired catalyst are acquired. Moreover, OH contained in the total quantity and alkali chemicals of each metal ion of Zn, aluminum, and Mg in the metal ion content liquid at the time of catalyst precursor preparation - Especially similarly about a ratio with the total quantity of ion and An-ion it is not limited.

[0011] Metal ion content liquid and alkali chemicals are supplied to a predetermined reaction vessel, stirring mixing is carried out, and both precipitation reaction performs preparation of a catalyst precursor. It is desirable to carry out from a viewpoint of the catalyst engine performance, adding metal ion content liquid and alkali chemicals to coincidence, adjusting the addition rate of alkali chemicals, and keeping pH of mixed liquor constant. As a pH value kept constant, it is desirable to set up in pH=9-11. From a viewpoint of catalytic activity, preferably, more preferably, this precipitation reaction is -15-10 degrees C preferably, and is performed especially -20-20 degrees C still more preferably 30 degrees C or less 45 degrees C or less for about 1 to 5 hours. Subsequently, supply of metal ion content liquid and alkali chemicals is suspended by request for about 1 to 20 hours, and it ripes on the same conditions as a precipitation reaction.

[0012] the catalyst precursor which separated from the solvent metal ion content liquid and the catalyst precursor obtained by mixing of alkali chemicals by approaches, such as filtration and centrifugal separation, and was obtained -- water -- it washes using ion exchange water preferably. 100 degrees C or more of the target catalysts are more preferably acquired by calcinating 400-1000 degrees C at 500-800 degrees C especially preferably, and considering as a multiple oxide preferably [make it dry at 80-120 degrees C after washing, and] in an inert gas air current and air or under a vacuum. It cools in inert gas or a vacuum, and, as for the catalyst after baking, it is desirable after cooling to be immersed in the active hydrogen compound used for a reaction or AO adduct in order to prevent adsorption of water or a carbon dioxide.

[0013] It can also use by using a catalyst as a Plastic solid again. Shaping receives a catalyst or a catalyst precursor. As a binder for shaping Only water Or water, alumina sol, a silica sol, an

antimony sol, a titanium sol, One or more sorts of the inorganic binders or ethanol chosen from the group of a zirconia sol, A water solution with organic binders, such as a methanol, ethylene glycol, a glycerol, and fatty alcohol It is preferably carried out especially by adding 0.5 to 30% of the weight preferably 0.5 to 40% of the weight 50 or less % of the weight among the mixture of a catalyst or a catalyst precursor, and the binder for shaping. Kneading with the binder for shaping can be performed, for example using a well-known kneader etc., and can perform shaping, for example with well-known extrusion molding, making tablet shaping, etc. It dries and calcinates on the above-mentioned conditions after shaping.

[0014] AO addition reaction said to <AO addition reaction> this invention means the reaction for which AO is made to add to an active hydrogen compound. The catalyst of this invention has high catalytic activity, and it may raise labile and selectivity in this AO addition reaction. Since labile can be maintained sufficiently highly, the amount of the catalyst used in reaction time can be lessened, and the load to a catalyst separation process can be reduced. Furthermore, since the selectivity of AO addition reaction is high, the amount of generation of the high molecular-weight object (polyethylene glycol) as a by-product can be reduced sharply.

[0015] As an active hydrogen compound used for AO addition reaction, one or more sorts of alcohols, phenols, polyols, carboxylic acids, thiols, amines, and amides are mentioned. In these, alcohols are desirable, as these alcohols, the first class of the straight chain of carbon numbers 2-30 or branched chain or the second class alcohol is desirable, and the first-class alcohol of carbon numbers 6-24 is more desirable. Specifically, lauryl alcohol, myristyl alcohol, palmityl alcohol, stearyl alcohol, etc. can be mentioned.

[0016] Moreover, although what kind of thing is sufficient as it as long as AO reacts with an active hydrogen compound and can generate an adduct, that [its] to which epoxidation of the carbon with which carbon numbers 2-8 adjoin was carried out is desirable, and ethyleneoxide (henceforth EO), propylene oxide, or especially such mixture are desirable.

[0017] Although any formats, such as a stirred-tank-type batch process, a stirred-tank-type circulation type, and a fixed-bed circulation type, can be used for it, the reactor of AO addition reaction has a desirable fixed-bed circulation type, if the complicatedness of catalyst separation recovery etc. is taken into consideration.

[0018] In use with a batch process reactor, the amount of the catalyst used of this invention has desirable 0.05 - 20 weight section to the active hydrogen compound 100 weight section, and its 0.1 - 8 weight section is usually more desirable. Since a product will decompose if too high [when too low, a reaction rate is slow, and], 80-230 degrees C of 120-180 degrees C of reaction temperature are 120-160 degrees C especially preferably more preferably. Although reaction pressure is based also on reaction temperature, it is 0.1 - 1MPa absolute pressure more preferably below 2MPa absolute pressure.

[0019] When it is powdered and uses a catalyst in AO addition reaction, an active hydrogen compound and a catalyst are taught by said ratio into a reactor, after introducing 0.1-100 mol of AO(s) and making them react preferably to one mol of active hydrogen compounds in nitrogengas-atmosphere mind under predetermined temperature and flow and pressure requirement, it can cool and AO adduct can be obtained by carrying out a catalyst a ** exception. moreover, when

use a catalyst as a Plastic solid, a shaping catalyst be put into the stirring aerofoil which have the basket made with the wire made from stainless steel etc., and this and an active hydrogen compound be teach to a reactor, and after introduce AO and make it react in nitrogen gas atmosphere mind under predetermined temperature and flow and pressure requirement, it can carry out by extract only AO adduct cool and generated.

[0020] In manufacturing AO adduct by the fixed-bed circulation formula, the reactor of for example, a fixed-bed circulation type is filled up with a catalyst, and it dips AO for AO and an active hydrogen compound as a rate of 0.1-10 mols preferably to one mol of active hydrogen compounds. As for a dipping rate, 0.1-100h-1 is desirable at liquid space velocity, 0.2-70h-1 is more desirable, and especially 1-50h-1 is desirable. Especially a coil pressure is good at well-known extent which is not limited and is usually carried out. Below 3MPa absolute pressure is specifically desirable, 0.2 - 2MPa absolute pressure is more desirable, and especially 0.2 - 1.6MPa absolute pressure is desirable. 50-300 degrees C of reaction temperature are desirable, its 80-250 degrees C are more desirable, and especially its 100-230 degrees C are desirable. low-grade as AO -- AO, in using especially EO, in order to avoid the danger of the explosion, it is desirable to carry out to the bottom of nitrogen-gas-atmosphere mind.

[0021] When it carries out by this fixed-bed circulation formula, the component metal of a catalyst is not contained in AO adduct obtained, but the separation processing by filtration, centrifugal separation, etc. of AO adduct and a catalyst is unnecessary for it in it after a reaction.

[0022] Moreover, in AO addition reaction using the conventional catalyst, by generation of the high molecular-weight object (polyethylene glycol) as a by-product, the solution viscosity of AO adduct which is the target product may increase remarkably, and the filterability of a catalyst was falling. the catalyst of this invention -- very much -- ** -- since the catalytic activity can be high and can reduce the amount of generation of a polyethylene glycol sharply in addition to the filterability of the catalyst itself [this] being good from a viewpoint of it being high, therefore being easy to pass filtrate, the filterability of a catalyst improves by leaps and bounds. In addition, filterable evaluation of a catalyst is performed in the measurement list of high molecular weight **** in a product by the following all directions methods.

[0023] The quantum of the polyethylene glycol in a <measuring method of high molecular-weight **** in product> AO adduct is analyzed with the extraction method in n-butanol saturated water. Analysis adds the solution which contained the polyethylene glycol in it using the mixed liquor (it separates into a bilayer) of n-butanol saturated water and a water saturation n-butanol solution, extracts a polyethylene glycol in a water saturation n-butanol solution, and asks for it by carrying out weighing capacity (g) of the sampling volume.

[0024] Filterable evaluation of the catalyst of <filterability evaluation of catalyst> this invention filters a catalyst by constant pressure filtration, and is performed to the obtained data with the application of the RUTH type [Ruth (Ruth), B.F., Ind.Eng.Chem., 27(1935) p.708] known as a constant-pressure-filtration type. the cake specifically obtained by RUTH plot -- specific resistance alpha (m/kg) is used for filterable evaluation. the following -- the constant-pressure-filtration type of RUTH, and a cake -- the derivation approach of specific resistance alpha is shown.

[0025] [The constant-pressure-filtration type of RUTH]

[0026]

[Equation 1]

[0027]

V : filtrate volume (m 3) A : Filtration area (m2)

Vo: the amount of virtual filtrate (m 3) P: Filtration pressure (kgf/m2)

theta: filtration time amount (hr) m: Cake **** mass ratio (-)

theta 0: V 0 Time amount to acquire (hr) s: Solid content concentration (-)

K:Ruth Constant-pressure-filtration constant (m 6 / hr) mu': Filtrate viscosity (kg and s/m 2)

alpha: cake Average specific resistance (m/kg) rho: Filtrate consistency (kg/m 3)

[0028] The constant-pressure-filtration type of RUTH is transformed and it is [0029].

[Equation 2]

$$\frac{d\theta}{dV} = \frac{2}{K} (V+V_0)$$

[0030] Here, it is K'=K/A2. It is [0031] when it carries out.

[Equation 3]

$$\frac{d\theta}{d(V/A)} = \frac{2}{K'}(V/A+V_{\bullet}/A)$$

[0032] (V/A) -- receiving -- d theta/d (V/A) the cake from the slope of a line plotted and obtained -- specific resistance alpha is computable. a cake -- specific resistance alpha is 4x1010 or less m/kg preferably from a viewpoint that suitable catalyst filterability is acquired.

[0033]

[Example] Example 1 [catalyst preparation] Zn(NO3) 2 and 6H2 O 55.8g, aluminum(NO3) 3 and 9H2 O Mg(NO3) 2 and [112.5g and] 6H2 O The mixed solution which dissolved 144.2g in 1299g of ion exchange water 0.24 mol/L Na2 CO3 A water solution and 4Ns With the NaOH water solution, coincidence supply was carried out at the reaction vessel of 5L volume by the volume of 12.5 mL/min, 9 mL/min, and 5 - 7.5 mL/min, respectively. 500g of water is beforehand put into the reaction vessel, and it stirred by 250rpm with the fixed-speed stirrer. After it carries out temperature control of it so that whenever [solution temperature] may become 15**2 degrees C, it adjusted the addition of a NaOH water solution so that pH may be further set to 9.7-10.3, and it performed a precipitation reaction for 2 hours, reaction mixture suspends supply of each water solution, and it was ripened for 1 hour, with suspension stirred. This suspension was filtered and the obtained white solid-state was fully washed using ion exchange water. The catalyst precursor of the shape of a white solid-state which is dried in a 110-degree C warm air oven after washing for 12 hours, and is expressed with following type:[(Zn0.25Mg0.75) 5/7 aluminum2/7 (OH)2] (CO3) 1/7, and cH2 O was obtained. Subsequently, it is a catalyst precursor after desiccation N2 In the air current, it calcinated for 2 hours and 550 degrees C of catalysts were acquired.

[0034] [Manufacture of AO adduct] AO adduct was manufactured using the above-mentioned catalyst. 3. After nitrogen permuted the inside of 1 weight section preparation and a system to these 100 alcoholic weight sections, the temperature up of the catalyst acquired with lauryl alcohol (trade name: cull call 2098, Kao Corp. make) 500g was carried out to 5L ** autoclave to 160 degrees C, carrying out fixed-speed stirring by 400rpm. It is EO at this temperature. It introduced maintaining 355g at pressure 0.1MPa absolute pressure, and reacted. Labile was three mol-EO/(mol-alcohol andh). It cooled at 110 degrees C, constant pressure filtration of the catalyst was carried out on condition that the following, and it dissociated with AO adduct. the cake of a catalyst for which this constant-pressure-filtration data was asked with the application of the RUTH type -- specific resistance was 3.2x1010 m/kg. Moreover, the number of EO average addition mols of high molecular weight **** in obtained AO adduct was 3 0.73% of the weight.

[0035]

<Constant-pressure-filtration conditions> Filtration temperature: 110 degrees C Filtration pressure: 98kPa Filtration area: 6.16cm2 Filter cloth: FTby Shikishima canvas company7501SS [0036] Except setting an example 2 and 3Zn(NO3) 2 and 6H2 O, and Mg(NO3) 2 and 6H2 O to 33.5g, 163.5g (example 2), or 22.3g and 173.1g (example 3), respectively, the catalyst was prepared like the example 1, the same actuation as an example 1 was performed using the acquired catalyst, and AO adduct was obtained. A result is shown in Table 1 and 2.

[0037] Example of comparison 1Mg(NO3) 2, and 6H2 O It is the mixed solution which dissolved 192.3g, and aluminum(NO3) 3 and 9H2 O120.8g in 1315g of ion exchange water 0.24 mol/L Na2 CO3 A water solution and 4Ns With the NaOH water solution, coincidence supply was carried out at the reaction vessel of 5L volume by the volume of 12.5 mL/min, 9 mL/min, and 5 - 7.5 mL/min, respectively. 500g of water is beforehand put into the reaction vessel, and it stirred by 250rpm with the fixed-speed stirrer. After it carries out temperature control of it so that

whenever [solution temperature] may become 15**2 degrees C, it adjusted the addition of a NaOH water solution so that pH may be further set to 9.7-10.3, and it performed a precipitation reaction for 2 hours, reaction mixture suspends supply of each water solution, and it was ripened for 1 hour, with suspension stirred. This suspension was filtered and the obtained white solid-state was fully washed using ion exchange water. After washing, it was made to dry in a 110-degree C warm air oven for 12 hours, and the white solid-state-like catalyst precursor was obtained. It is a catalyst precursor after desiccation N2 In the air current, it calcinated for 2 hours and 550 degrees C of catalysts were acquired. The same actuation as an example 1 was performed using the acquired catalyst, and AO adduct was obtained. A result is shown in Table 1 and 2.

[0038] Using the catalyst (1.25Mg (OH) 2, aluminum(OH)3, xCO3, and yH2 O) indicated by the example 1 of example of comparison 2 JP,8-268919,A, this catalyst was calcinated like said example 1, and the catalyst oxide was prepared. The same actuation as an example 1 was performed using this catalyst oxide, and AO adduct was obtained. A result is shown in Table 1 and 2.

[0039] Example of comparison 3Zn(NO3) 2, and 6H2 O 223g, aluminum(NO3) 3 and 9H2 O About the mixed solution which dissolved 112.5g in 1300g of ion exchange water, it is 0.24 mol/LNa2 CO3. A water solution and 4Ns With the NaOH water solution, coincidence supply was carried out at the reaction vessel of 5L volume by the volume of 12.5 mL/min, 9 mL/min, and 5 - 7.5 mL/min, respectively. 500g of water is beforehand put into the reaction vessel, and it stirred by 250rpm with the fixed-speed stirrer. After it carries out temperature control of it so that whenever [solution temperature] may become 15**2 degrees C, it adjusted the addition of a NaOH water solution so that pH may be further set to 9.7-10.3, and it performed a precipitation reaction for 2 hours, reaction mixture suspends supply of each water solution, and it was ripened for 1 hour, with suspension stirred. This suspension was filtered and the obtained white solidstate was fully washed using ion exchange water. After washing, it was made to dry in a 110degree C warm air oven for 12 hours, and the white solid-state-like catalyst precursor was obtained. It is a catalyst precursor after desiccation N2 In the air current, it calcinated for 2 hours and 550 degrees C of catalysts were acquired. The same actuation as an example 1 was performed using the acquired catalyst, and AO adduct was obtained. A result is shown in Table 1 and 2.

[0040]

[Table 1]

		触媒前駆体組成式
実施例	1	[(Zn _{0. 25} Mg _{0. 75}) _{5/7} Al _{2/7} (OH) ₂](CO ₃) _{1/7} • cH ₂ O
	2	$[(Zn_{0.15}Mg_{0.85})_{5/7}Al_{2/7}(OH)_{2}](CO_{3})_{1/7} \cdot dH_{2}O$
	3	$[(Zn_01Mg_09)_{5/7}Al_{2/7}(OH)_2](CO_3)_{1/7} \cdot eH_2O$
比較例	1	Mg _{12/17} Al _{5/17} (OH) ₂ (CO ₈) _{0.5} • fH ₂ O
例 例	2	1.25Mg(OH) ₂ A1(OH) ₃ · xCO ₈ · yH ₂ O
	3	$Zn_{5/7}Al_{2/7}(OH)_2(CO_3)_{0.5} \cdot 2.7H_2O$

表中、触媒前駆体組成式におけるH₂0 の係数はそれぞれ0より大きい数を示す。

[0041]

[Table 2]

		(Zn+Mg)/A1 原子比	Zn/Mg 原子比	A O付加反応の 反応活性 [mol-BO/(mol-アルコール・h)]	AO付加体中の 高分子量体 [重量%]	原料中の 未反応 アルコール [重量%]	ケーク比 抵抗α [×10 ¹ m/kg]
実施例	1	2.5	0. 33	3. 0	0.73	2.7	3. 2
	2	2.5	0.17	3. 1	1.6	2.4	3. 4
	3	2.5	0.11	3. 1	2.1	3.2	3. 1
比較例	1	2.4	_	3. 1	2.8	5. 2	9. 9
	2	1.25	_	2. 8	2.3	5.1	8. 2
	3	2.5	_	0. 4	3. 5	3.2	22. 0

[0042] The catalyst of this invention which consists of a multiple oxide of Zn, aluminum, and Mg likes the unreacted part of the alcohol which is a raw material, can do it by there being nothing, and moreover, it excels in catalytic activity and it is [there are few amounts of

byproductions of a high molecular weight object, and] excellent also in filterability so that clearly from Table 2.

[0043]

[Effect of the Invention] According to this invention, the catalyst for AO addition reactions which catalytic activity can be high compared with the conventional catalyst, and can reduce sharply the amount of generation of the high molecular weight object as a by-product, consequently can raise the filterability of a catalyst by leaps and bounds is acquired, and very efficient quality AO adduct can be manufactured compared with the conventional technique.

[Translation done.]